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# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Pulping Process

We, BUCKMAN LABORATORIES, INC., a corporation organised and existing under the laws of the State of Tennessee, United States of America, having its principal place of business at 1256 North Mclean Boulevard, Memphis, Tennessee 38108, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of chemical pulp from cellulosic materials by digesting the cellulose materials in an aqueous solution with a pulping chemical e.g. as in the sulfate and sulfite processes. More particularly, the present invention constitutes an improvement over known processes of producing chemical pulp by digesting cellulosic materials such as wood chips by the sulfate and sulfite processes.

Since the methods of producing chemical pulp by the sulfate and sulfite processes are well known by those skilled in the art, a description thereof will not be repeated here. For a detailed description of these processes, reference is made to Sven A. Rydholm, "Pulping Processes," Interscience Publishers; New York, London and Sydney, 1965, particularly pages 576—649; and Pulp and Paper Science and Technology, Vol. I, Pulp, edited by C. Earl Libby, McGraw-Hill Book Co., New York, 1962, particularly chapters 9 and 10 thereof. As used herein, the term "sulfite process" includes bisulfite and sulfite processes utilizing ammonium, alkali- and alkaline-earth-metal bisulfite or sulfite solutions under mildly alkaline, neutral or acidic conditions.

Although large quantities of chemical pulp are prepared by the sulfite process, this process possesses a number of inherent disadvantages. For example, the sulfite industry is very sensitive to the wood raw material

that may be used. Additional disadvantages reside in the difficulty of recovering the cooking chemicals and utilizing the waste products which correspond to about one-half the wood substance. Obviously, if the chemicals are not recovered, means must be found for their disposal. The disposal of these waste liquors is a direct burden upon the sulfite economy, a factor often accentuated by laws prohibiting the disposal of these liquors in public waters. Although most wood species may be pulped by the sulfate process, the process is not entirely satisfactory. For example, the capital investment required per unit of production is very large.

The present invention is based upon the discovery that the N,N-dimethylamides of straight chain aliphatic carboxylic acids are useful as a cooking aid during the digestion of cellulosic material with pulping chemicals as for example in the kraft and sulfite processes (the kraft process being a method of preparing a pulp, commonly a strong pulp from pine, by the sulfate process), and that the use of such N,N-dimethylamides as a cooking aid thus gives rise to improved processes for the preparation of chemical pulp.

According to the present invention, there is provided a process for the preparation of a chemical pulp from cellulosic material in which the cellulosic material is digested in an aqueous solution containing a pulping chemical at an elevated temperature, the N,N-dimethylamide of at least one straight chain aliphatic carboxylic acid containing 18 carbon atoms being incorporated in the said aqueous solution as a cooking aid. The digestion step may be carried out under mildly alkaline, neutral or acidic conditions.

Suitable N,N-dimethylamides of straight-chain carboxylic acids are ones prepared from carboxylic acids containing 18 carbon atoms. Preferred acids are further characterized by

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- having at least one carbon to carbon double bond, because such acids and the N,N-dimethylamides thereof are normally a liquid which is an aid in handling. It should be understood, however, that a saturated acid such as stearic may be used to prepare an efficient N,N-dimethylamide cooking aid. Generally, we prefer not to use the saturated acids because both the acid and the dimethylamide are solids at normal temperatures, causing handling difficulties. Furthermore, the melting points of the N,N-dimethylamides of the saturated acids are relatively high and, as a consequence, these amides tend to form deposits in the papermaking system with a drop in temperature. Specific preferred acids include: oleic, linoleic, linolenic, ricinoleic, and mixtures thereof. Also suitable are the mixed acids found in tall, castor, corn, cottonseed, linseed, olive, peanut, rapeseed, safflower, sesame, and soybean oils which, of course, produce a mixture of N,N-dimethylamides. A mixture of carboxylic acids particularly suitable for use in our invention is that available for use in our invention is that available commercially as tall oil fatty acids under the trademark Unitol ACD. A typical analysis of this product is as follows:—

TABLE 1

	Specification range	Typical analysis
Fatty acids, %	98.8 — 99.7	98.9
Rosin acids, %	0.2 — 0.6	0.5
Unsaponifiables, %	0.1 — 0.6	0.6
Linoleic acid, %		45
Oleic acid, %		51
Saturated acid, %	2.0 — 2.8	2.4
Acid number	198 — 201	199
Saponification number	198 — 202	200
Color, Gardner	3— — 4—	3+
Viscosity		
S.S.U.,* 100°F.		105 (21.7 centistokes)
Gardner seconds		0.9
Specific gravity, 60°F./60°F.		0.905
Titre, °C.	-1 — 1.0	0.0
Flash point, °F.		375
Fire point, °F.		435

(\*1 Saybolt Universal Second (S.S.U.) = 4.6347 centistokes at 100°F. or 4.6673 centistokes at 210°F).

- When the N,N-dimethylamide or a mixture thereof is used as a cooking aid in conjunction with the sulfite process for preparing chemical pulp, the dimethylamide may be conveniently and preferably added continuously into the high-pressure acid accumulator. Since most high-pressure accumulators are equipped with a recirculating pump which continuously recirculates the sulfite solution, the N,N-dimethylamide may be added to the suction or to the discharge line of the pump. If the high-pressure accumulator is not provided with a recirculating pump, the N,N-dimethylamide may be added to the low-pressure acid accumulator or to the raw acid storage tank. As another alternative, the N,N-

dimethylamide may be siphoned into the cooking acid line going to the sulfite digester. When this procedure is followed, care must be taken to assure even distribution of the N,N-dimethylamide throughout the cooking acid. The concentration of N,N-dimethylamides actually used in the cooking process is not necessarily equal to the amount of the N,N-dimethylamide added to the system over the amount of cellulose fiber cooked during a given time. Since it is a practice to effect a side relief of the cooking acid back to the high pressure accumulator of 20–65 percent of the volume of acids pumped to the digester, then the concentration of the N,N-dimethylamide in the acid after equilibrium has been reached may be several times that obtained in a single cook evaluation. In the kraft process, the N,N-dimethylamide or a mixture of such amides may be added to the white liquor going to the digester.

As to the amount of the N,N-dimethylamide to be added to the aqueous system, suitable and preferred quantities vary from 50 to 2,000 parts and 400 to 1,200 parts per million parts of moisture-free cellulose fiber, respectively. It will be understood, of course, that larger quantities of the N,N-dimethylamide may be used with no detrimental effect, but such larger quantities increase the costs of operation with limited material benefit.

We have found that the N,N-dimethylamides may be added to all types of sulfite systems, such as the conventional calcium (lime), milk of lime, sodium, magnesium and ammonia base acid sulfite pulping with highly beneficial results. In brief, the desirable results obtainable by following the teachings of our invention may be summarized as follows:

1. Increased yield of usable or saleable fiber per unit of wood. Specifically, a normal yield of unbleached pulp (so-called high-yield pulps as produced in newsprint mills) is about 45 percent based on the moisture-free weight of the wood. Under the same conditions, the presence of the N,N-dimethylamide as a cooking aid increased the yield of unbleached pulp to more than 49 percent.
2. Reduced consumption of cooking chemicals, such as sulfur, sodium, calcium, magnesium, and ammonia. This in itself serves to alleviate the problem of waste liquor disposal.
3. Increased production per unit of equipment.
4. Reduction in the quantity of rejects.
5. Reduction in pitch content.

6. Increase in overall mill efficiency in that a larger quantity of fiber of a higher quality is produced at a lower production cost.

7. Steam savings. Both cooking time and temperature are reduced.

8. Increase in brightness, particularly in high yield mills.

9. Improved paper machine performance in that the dimethylamides have a desirable effect on papermill lumping problems, because such lumps are usually high in sulfite fiber content.

In order to disclose the nature of the present invention still more clearly, the following illustrative examples will be given.

#### EXAMPLE 1

In this example, two runs were made:

Run No. 1 was a conventional bisulfite digestion of coniferous wood chips for the production of chemical pulp to be used for long fibers in the manufacture of newsprint as a control, and Run No. 2 was a duplicate of No. 1 with the exception that a mixture of N,N-dimethylamide was used as a cooking aid. The results of Run No. 1 are averages of data compiled during the six weeks prior to the trial Run No. 2. The results of Run No. 2 are averages of results obtained during the six days of trial Run No. 2.

In Run No. 1, 43 tons of air-dry coniferous wood chips were added to the digester and digested using sodium bisulfite prepared by bubbling SO<sub>2</sub> through an aqueous soda ash solution as the cooking acid. Approximate specifications of the cooking acid were 3.6 percent total and combined SO<sub>2</sub> at pH 4. The digesting procedure was as follows: Temperature raised to 90°C. over a period of 30 minutes, held at that temperature for 1 hour, then raised to 145°C., and maintained at the latter figure for 5 hours. At the end of the 5-hour digesting period, the digester was blown and the contents discharged, product washed with water, cleaned, and dewatered.

In Run No. 2, the procedure of Run No. 1 was repeated with the exception that a mixture of N,N-dimethylamides of tall oil fatty acids was added to the digester at the beginning of the cooking in an amount equal to 800 parts per million parts of moisture-free cellulose fiber. The analysis of the tall oil fatty acids used to prepare the mixture of N,N-dimethylamides used is given in table 1. A comparison of the control and the N,N-dimethylamides bisulfite cooks is summarized in table 2.

TABLE 2

	Control	N,N-dimethyl- amides used as cooking aid
Centri-Cleaner (the word Centri-Cleaner is a registered Trade Mark) rejects, %	1.4	0.95
Slivers in stock,* %	0.87	0.58
Sulfite brightness, % GE	54.4	54.9
Pitch content, %	1.4	1.0
Sulfur consumption, lb./ton of pulp	155	131
Soda ash consumption, lbs./ton of pulp	258	218

\*Long slender pieces of fibres in the stock solution.

#### EXAMPLE 2

The effectiveness of the mixture of N,N-dimethylamides prepared from Unitol ACD tall oil fatty acids as a cooking aid in reducing cooking time was determined by comparing the results obtained by carrying out a series of cooks in the presence of the dimethylamide to similar cooks in the absence of the dimethylamide.

The particular mill at which this test was conducted has four digesters and produces approximately 10 tons (1 ton = 907 kilograms) of air-dried (10% H<sub>2</sub>O) cooked sulfite cellulose pulp per cooking cycle or "blow." Normal production (no dimethylamide used) has been 12 to 13 cooks (blows) per day, using a cooking cycle as follows:

- 1.0 hour from capping digester to 110°C.
- 1.25 hours from 110°C. to 163°C.
- 3.25 hours at 163°C. (normal cooking temperature)

Total cooking time: 5.5 hours

The cooking acid used was a magnesium base sulfite liquor containing 5.2 percent total SO<sub>2</sub> with a pH of about 3.8.

In this series of cooks, a mixture of the dimethylamides as identified above was added to the cooks in an amount equal to 800 parts per million parts of air-dried pulp. It was found that the use of the dimethylamide cooking aid made it possible to reduce the cooking time from 5.5 to 4.75 hours. This reduction in cooking time was obtained with no sacrifice in yield or quality of the final sulfite cellulose pulp. Overall production was increased to an average of 14 to 15 cooks per day.

The results obtained in example 2 as compared to those in example 1 were as follows:

1. Reduced cooking time
2. Reduced acid consumption
3. Reduced rejects
4. Reduced pitch content of the pulp

5. Pitch did not deposit on screen plates
6. Easier screening
7. Increased yield (more tons per blow)
8. Increased production (more tons per blow, more blows per day)
9. Improved pulp strength as measured by bursting test and tearing test.

#### EXAMPLE 3

The procedures of examples 1 and 2 were repeated in which the N,N-dimethylamides of the mixed acids found in castor, corn, cottonseed, linseed, olive, peanut, and soybean oils were used instead of the N,N-dimethylamides of tall oil fatty acids. The results were similar to those obtained in examples 1 and 2.

We have also found that the advantageous results of our invention are attained when the N,N-dimethylamides of the carboxylic acids listed are used as a cooking aid in aqueous ammonium, alkali and alkaline-earth metal bisulfite and sulfite solutions under either mildly alkaline, neutral, or acidic conditions.

#### EXAMPLE 4

In this example, two runs were made:

Run No. 1 involved the digestion of hardwood chips for the production of chemical pulp to be used for fibers in the manufacture of corrugating medium by a conventional continuous process operating at a production rate of 220 tons of pulp per day. Digestion conditions were as follows: pressure 150 p.s.i.g., temperature 366°F., and a reaction time of 16 minutes. The cooking liquor which contained 1 pound of sodium sulfite and 0.45 pound of sodium carbonate per gallon was added to the digester at a rate of 37 gallons per minute. Consistency in the primary refiners was about 28 percent and in the secondary refiners it ranged from 4.6 to 5.1. Freeness average about 465 (Canadian Standard) out of the secondary refiners.

In Run No. 2, the procedure of Run No. 1 was repeated with the exception that a mixture of tall oil fatty acids (same as used in Run No. 2 of example 1) was introduced into the cooking liquor on the intake side of the pump delivering the liquor to the digester at a rate of about 300 parts per million parts of moisture-free cellulose fiber.

It was found that the addition of the dimethylamides to the digester reduced power consumption by about 15 percent and increased the production of chemical pulp by about 15 percent with no sacrifice in yield or quality of the final chemical pulp.

#### EXAMPLE 5

The effectiveness of the mixture of N,N-dimethylamides prepared from Unitol ACD tall oil fatty acids as a cooking aid in reducing cooking time, thus increasing production in continuous digestion process (kraft process), was determined by comparing the results obtained by carrying out the cooking process in the absence of the dimethylamides (Run No. 1) to a similar cooking process in the presence of the dimethylamides (Run No. 2).

In Run No. 1, about 300 tons per day of air-dry chips consisting of about 60 percent mixed pines including ponderosa, sugar, western white, and lodge pole pine; 25 percent Douglas-fir; and 15 percent white fir was added to the continuous digester and digested using a cooking liquor containing active alkali, 1.5 pounds per cubic foot; effective alkali, 1.3 pounds per cubic foot; and a sulfidity of 20 percent. Forgoing numerical values are as measured in the cooking zone. Total alkali in the white liquor used for makeup was 7.2 pounds per cubic foot. Cooking conditions were as follows: Temperature in the second zone of the digester, 280°F., increased to 350°F.; and in the third zone (where cooking actually takes place), 350°F. Contact time in the third zone was 45 minutes. The liquor consistency or ratio of the cooking liquor to wood at the discharge of the digester was 18.5 percent. There was a circulation rate of 325 gallons per minute of cooking liquor in the third zone, of which 90 gallons per minute was made up from fresh white liquor.

In Run No. 2, the procedure of Run No. 1 was repeated with the exception that a mixture of tall oil fatty acids (same as used in Run No. 2 of example 1) was introduced into the cooking liquor on the intake side of the pump delivering the liquor to the digester at a rate of about 800 parts per million parts of moisture-free cellulosic fiber.

It was found that the addition of the dimethylamides to the digester increased the rate at which the chemical pulp was produced by about 12 percent with no sacrifice in yield or quality of the final chemical pulp.

In addition, the use of the dimethylamides as a cooking aid inhibited scale formation

both in the digesters and in the heaters located outside the digesters. This result was apparent from the fact that in Run No. 1 it was necessary to remove the scale formed in the heaters after 1.5 days' operation, while in Run No. 2 where the dimethylamides were used, the heaters could be operated for a period of 7 days before the necessity of scale removal.

Beneficial results are also attained when the N,N-dimethylamides as disclosed herein are added to other processes such as the soda process of producing chemical pulp and the production of groundwood from bolts or chips after chemical impregnation followed by defibering with conventional stone grinders or disc refiners or various modifications thereof.

#### WHAT WE CLAIM IS:—

1. A process for the preparation of a chemical pulp from cellulosic material in which the cellulosic material is digested in an aqueous solution containing a pulping chemical at an elevated temperature, the N,N-dimethylamide of at least one straight chain aliphatic carboxylic acid containing 18 carbon atoms being incorporated in the said aqueous solution as a cooking aid.
2. A process as claimed in claim 1 wherein the cellulosic material is digested according to the sulfite process.
3. A process as claimed in claim 1 wherein the cellulosic material is digested according to the kraft process as herein defined.
4. A process as claimed in claim 2 wherein the pulping chemical is ammonium, alkali- or alkaline-earth-metal bisulfite or sulfite.
5. A process as claimed in any of the preceding claims wherein the said straight chain carboxylic acid contains at least one carbon to carbon double bond.
6. A process as claimed in any of claims 1 to 4 wherein the said aqueous solution has the N,N-dimethylamide of oleic acid incorporated therein.
7. A process as claimed in any of claims 1 to 4 wherein the said aqueous solution has the N,N-dimethylamide of linoleic acid incorporated therein.
8. A process as claimed in any of claims 1 to 4 wherein the said aqueous solution has the N,N-dimethylamide of linolenic acid incorporated therein.
9. A process as claimed in any of claims 1 to 4 wherein the said aqueous solution has the N,N-dimethylamide of ricinoleic acid incorporated therein.
10. A process as claimed in claim 5 wherein the said aqueous solution has the N,N-dimethylamides of a mixture of straight chain aliphatic carboxylic acids containing 18 carbon atoms and at least one carbon to carbon double bond incorporated therein.
19. A process as claimed in claim 18 wherein the said mixture of acids is derived from tall oil.

- 5 12. A process as claimed in claim 10 wherein the said mixture of acids is derived from corn oil.
13. A process as claimed in claim 10 wherein the said mixture of acids is derived from cottonseed oil.
- 10 14. A process as claimed in claim 10 wherein the said mixture of acids is derived from linseed oil.
- 15 15. A process as claimed in claim 10 wherein the said mixture of acids is derived from peanut oil.
16. A process as claimed in claim 10 wherein the said mixture of acids is derived from soybean oil.
- 20 17. A process as claimed in any of the preceding claims wherein the said aqueous solution has at least 50 parts per million by weight based on the cellulosic material (dry weight) of the N,N-dimethylamide incorporated therein.
- 25 18. A process as claimed in claim 17 wherein the said aqueous solution has from 50 to 2,000 parts per million by weight based on the cellulosic material (dry weight) of the N,N-dimethylamides incorporated therein.
- 30 19. A process as claimed in claim 18 wherein the said aqueous solution has from 400 to 1,200 parts per million by weight based on the cellulosic material (dry weight) of the N,N-dimethylamide incorporated therein.
- 35 20. A process as claimed in claim 4 in which the cellulosic material is digested under mildly alkaline, neutral or acidic conditions, the said aqueous solution having at least 100 parts per million by weight based on the cellulosic material (dry weight) of the N,N-dimethylamide incorporated therein.
21. A process as claimed in claim 20 in which the N,N-dimethylamide is as defined in any of claims 5 to 9.
22. A process as claimed in claim 20 in which the said aqueous solution has the N,N-dimethylamides of a mixture of straight chain aliphatic carboxylic acids as defined in any of claims 10 to 16.
23. A process as claimed in any of claims 20 to 22 in which the said aqueous solution has from 200 to 1200 parts per million by weight based on the cellulose material (dry weight) of the N,N-dimethylamide incorporated therein.
24. A process as claimed in claim 1 substantially as herein described.
25. A process as claimed in claim 1 substantially as herein described in any of the Examples.
26. Chemical pulp when prepared by a process as claimed in any of the preceding claims.
27. Chemical pulp when prepared by a process as claimed in any of claims 20 to 23.
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